FY 2006 Annual Report

Coupled Biogeochemical Processes Governing the Stability of Bacteriogenic Uraninite and Release of U(VI) in Heterogeneous Media: Molecular to Meter Scales

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1. Objectives

In-situ reductive biotransformation of subsurface U(VI) to U(IV) (as "UO_2") has been proposed as a bioremediation method to immobilize uranium at contaminated DOE sites. The chemical stability of bacteriogenic "UO_2" is the seminal issue governing its success as an *in-situ* waste form in the subsurface. The structure and properties of chemically synthesized UO_{2+x} have been investigated in great detail[1-3]. It has been found to exhibit complex structural disorder, with nonstoichiometry being common, hence the designation "UO_{2+x}", where $0 < x < 0.25$. Little is known about the structures and properties of the important bacteriogenic analogs, which are believed to occur as nanoparticles in the environment. Chemically synthesized UO_{2+x} exhibits an open fluorite structure and is known to accommodate significant doping of divalent cations[4-6]. The extent to which bacteriogenic UO_{2+x} incorporates common ground water cations (*e.g.*, Ca^{2+}) has not been investigated, and little is known about nonstoichiometry and structure defects in the bacteriogenic material. Particle size, nonstoichiometry, and doping may significantly alter the reactivity, and hence stability, of bacteriogenic UO_{2+x} in the subsurface. The presence of associated sulfide minerals, and solid phase oxidants such as bacteriogenic Mn oxides may also affect the longevity of bacteriogenic UO_2 in the subsurface.

The objectives of this multi-institution project are to characterize the molecular scale structures, stability, and dissolution kinetics of bacteriogenic U(IV) products produced under conditions representing those in contaminated environments. Structure-property relationships will be deduced and their impact on UO_2 stability at the meter-scale will be assessed in column-scale measurements. Project partners include R. Bencheikh-Latmani (EPFL, synthesis of bacteriogenic UO_2 and column measurements), D. Giammar (WUStL, solubility and dissolution kinetics of bacteriogenic UO_2), and B. Tebo (OHSU, Oxidation kinetics of bacteriogenic UO_2 in the presence of Mn oxidizing bacteria). Each of these partners is the P.I. on a linked ERSP grant.

The objective of the SSRL portion of this linked effort is to characterize the atomic- and nano-scale structures of bacteriogenic UO_{2+x} produced by a variety of bacteria, including cultures from field sites, using a complementary suite of *in-situ* techniques. The local atomic structure around U and cation dopants will be measured using extended x-ray absorption fine-structure spectroscopy (EXAFS) and wide-angle x-ray scattering pair-distribution function analysis (WAXS-PDF). Unit cell constants will be measured using *in-situ* WAXS-Rietveld. Small angle x-ray scattering (SAXS) will be used to measure particle size distributions *in-situ*. This work will be complemented by WANS (wide-angle neutron scattering) analyses to define oxygen defects

in the unit cell. This DOE-funded project will provide a chemical basis for understanding the properties of nanoparticulate bacteriogenic UO_{2+x} in the subsurface and will identify methods to enhance its stability in bioremediation technologies.

2. Progress and Implications

This report summarizes work after year 1 (8 months in year 1) of a 3 year project. A post-doctoral researcher, Dr. Eleanor Schofield, was hired to work on the project in June 2006. Dr. Schofield is an outstanding addition to the team as she has extensive experience in synchrotron-based x-ray scattering techniques.

In-situ WAXS measurements of wet undoped bacteria-UO_{2+x} mixtures were measured in July 2006 at SSRL BL 2-1. The patterns exhibit broad peaks characteristic of a nanoparticulate phase. Unit cell refinements yield a lattice constant of 5.47(1) Å, which is significantly larger than the published value of 5.4297 Å, and a particle size estimate of ~3 nm. We tentatively attribute the relatively large unit cell constant to nano-induced expansion of the lattice. EXAFS data measured from undoped bacteriogenic UO_{2+x} show the presence of a U-O shell at *ca* 1.70 Å (in addition to the U(IV)-O shell at 2.36 Å), indicating the presence of U(VI). The 1.70 Å distance agrees with values reported for nonstoichiometric abiotic UO_{2+x}[2]. Samples were carefully protected from air prior to and during sample analysis, so this feature should not be ascribed to air-oxidation of the sample. Furthermore, EXAFS measurements of control samples, in which bacteriogenic UO_{2+x} was allowed to oxidize in air, indicate the presence of the trans-dioxo uranyl cation (UO_2^{2+}) with the typical 1.80 Å U(VI)-O distance. We attempted to fit this 1.80 Å shell into the EXAFS data for our bacteriogenic UO_{2+x}, but were unsuccessful because this frequency is not present in the data. Therefore, we tentatively conclude that bacteriogenic UO_{2+x} is able to support a non-stoichiometric structure. Such a structure would be expected to have a lower stability, and hence higher reactivity in the subsurface than pure UO_2, due to strain in the material. Further measurements are required to confirm or deny this hypothesis.

3. Planned Activities

To provide a comprehensive picture of the atomic and nano-scale structures of bacteriogenic UO_{2+x}, we will utilize a suite of complementary techniques to address the following structural aspects:

Oxidation state: Linear combinations of XANES spectra from $UO_{2.00}$ (obtained from D. Clark, LANL) and U(VI) models (autunite, schoepite, U(VI) nitrate, andersonite) will be fit to sample spectra to estimate U oxidation state.

Long range order of the uranium sublattice in bacteriogenic UO_{2+x}: in-situ transmission WAXS data will be measured at SSRL beam line 2-1 up to q = 12 Å^{-1} to screen samples for phases present. WAXS data will be measured to q = ~27 Å^{-1} at BL 10-2. Rietveld analysis will be used to establish unit-cell constants. Atomic position refinement is not planned at this time because of the breadth of peaks, which complicates refinement. PDF analysis will be conducted to probe pair correlations in the material.

Short range order; U-O and U-U pair correlations: EXAFS spectra will be measured to establish the local structure around U in bacteriogenic UO_{2+x}. Spectra will be measured at 77 K to sharpen long-range structural features.

Short range order; local structure around dopant cations: EXAFS spectra will be measured to establish the local structure around cation dopants (Ca^{2+}, Fe(II), Mn(II)). XANES for Mg^{2+} will be measured at the ALS and compared to spectra for Mg^{2+} reference compounds.

Short range order; O-O pair correlations: wide-angle neutron scattering (WANS) data will be measured at the Los Alamos Neutron Scattering Facility to assess O-O pair correlations in bacteriogenic UO_{2+x}. The neutron scattering cross-sections of O and U are comparable. In comparison, x-ray scattering cross-sections for U are approximately 10-fold stronger than for O. Thus, WANS analysis can provide information on O-O distances with much greater certainty than WAXS. This information, which is obtained for all atom pairs in the sample, is highly complementary to EXAFS data, which probes only U-atom pairs.

Particle size & morphology: SAXS measurements will be performed at beam line 1-4 on wet bacteria-oxide assemblages to give particle size, morphology and distribution. HR-TEM will be used to assess particle morphology/size *ex-situ*. Particle size can also be assessed from Rietveld refinement of WAXS data.

References:

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[5] R. J. Finch and R. C. Ewing, Journal of Nuclear Materials **190,** 133-156 (1992).

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4. Information Access

No papers have been published yet. An overview of the work was presented in poster format at the workshop of the Environmental Remediation Science Program hosted by the Idaho National Laboratory on June 12-14, 2006 and at the Fall ERSP PI meeting at the Oak Ridge Institute for Science and Education, October 23-25, 2006.